

Killing microorganisms

The invention relates to a method of killing microorganisms in aqueous industrial systems or products for industrial applications based on water by adding to the system from 0.001 to 5% by weight of a water-soluble or water-dispersible polymer containing from 30 to 100 mol% of styrenesulfonic acid, 0 to 40 mol% of an N-vinylactam and/or N-vinylamine, and from 0 to 30 10 mol% of further free-radically polymerizable monomers as a biocidal additive. It further relates to a method of protecting articles by applying an antimicrobial, aqueous composition comprising such an additive.

15 The term microbiocide or biocide is used in a general sense for all substances having the capacity to kill microorganisms, and embraces antibiotics, chemotherapeutics, disinfectants, and fungicides. In a more specific sense the term embraces substances used in industrial or scientific applications for the purpose, 20 for example, of preserving polymers, paints, inks, paper or wood or for protecting industrial installations such as cooling water circuits. Further details are set out in "Microbiocides", Ullmann's Encyclopedia of Industrial Chemistry, 6<sup>th</sup> Edition, 2000 Electronic Release.

25 In industrial or scientific applications the normal requirements of a biocide, such as effective biocidal action without human toxicity, are accompanied by the requirement of very good performance properties. Biocides used in industrial applications 30 ought not to impair the properties of the product under protection and ought to retain their effect in the product even in the course of its subsequent processing. Thus, for example, during the spray drying of an acrylic dispersion containing a biocide, the biocidal effect ought not to be impaired, so that 35 even the dried powder or the redispersed powder is still protected by the biocide.

In aqueous dispersions, used for example to produce inks or coatings, it is common for the biocide used to comprise defined 40 substances of low molecular mass such as bronopol (2-bromo-2-nitro-1,3-propanediol), for example. Bronopol, however, may give rise to a slight yellow shade. In certain applications, moreover, a low total halogen content is desirable in order to avoid corrosion and yellowing problems. Furthermore, 45 high molecular mass biocides are advantageous in solid films in order to ensure a high long-term stability.

The use of polymers as biocides is known. For instance, DE-A 199 40 023, DE-A 199 52 221, and DE-A 199 55 992 disclose copolymers of aminopropyl vinyl ethers, acryloyloxyalkyldialkylamines or acryloyloxyalkylbenzophenone 5 ammonium salts, in each case with other ethylenically unsaturated monomers, as microbial protection for various industrial applications or for the coating of surfaces. Cationic polymers of this kind, however, are incompatible with customary ionically stabilized acrylate dispersions.

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It is also known that poly-4-styrenesulfonic acid or its salts can be used for various applications in the medical sector. US 6,239,182 discloses the use of sodium polystyrenesulfonates as vaginal contraceptives or for use against HIV. US 6,290,946 15 discloses the use of poly-4-styrenesulfonic acid or its derivatives in antibiotics. The use of polystyrenesulfonic acid and of styrenesulfonic acid copolymers as biocidal additives in the industrial sphere, on the other hand, has not been disclosed to date.

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It is an object of the present invention to provide a method of killing microorganisms in an aqueous environment using polymers. Such a method ought also to be employable in ionically stabilized dispersions without thereby adversely affecting the properties of 25 said dispersions.

We have found that this object is achieved by a method of killing microorganisms in aqueous industrial systems or products by adding to the system a biocidal additive, wherein the biocide is from 0.001 to 5% by weight of a water-soluble or 30 water-dispersible polymer containing - based in each case on the total amount of all monomer units present in the polymer -

- a) from 30 to 100 mol% of styrenesulfonic acid,
- 35 b) from 0 to 40 mol% of an N-vinylactam and/or N-vinylamine, and
- c) from 0 to 30 mol% of further free-radically polymerizable monomers

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and the sum of (a), (b), and (c) makes 100 mol%.

A second embodiment of the invention provides a method of protecting articles by applying an antimicrobial composition at 45 least comprising water or a predominantly hydrous solvent mixture and a biocidal additive to the article by means of an appropriate technique and removing water or the predominantly hydrous solvent

mixture, wherein the biocide is from 0.001 to 5% by weight of at least one water-soluble or water-dispersible polymer containing - based in each case on the total amount of all monomer units present in the polymer -

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- a) from 30 to 100 mol% of styrenesulfonic acid,
- b) from 0 to 40 mol% of an N-vinylactam and/or N-vinylamine, and
- 10 c) from 0 to 30 mol% of further free-radically polymerizable monomers

and the sum of (a), (b), and (c) makes 100 mol%.

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Details of the invention follow.

The invention relates to the use of certain biocidal additives in the nonmedical sector. Therapeutic or medical applications in or 20 on the human or animal body, and applications in crop protection, are not embraced by the present invention.

The term "aqueous industrial systems" for the purpose of this invention should be taken to include installations, especially 25 chemical installations, manufacturing installations or machinery, in which water or predominantly aqueous mixtures are used as auxiliaries or reaction media. Examples include reaction vessels, storage vessels, heating vessels, water refrigeration circuits, heat exchanger circuits, utility water circuits, ballast water 30 tanks or air conditioning units.

The term "products for industrial applications based on water" should be understood within the context of this invention to refer to water-based products which are employed in the 35 industrial, scientific, commercial, workshop or household sectors. The term also covers the segment of the food industry.

The term "water-based" or "based on water" has the meaning, as known in principle, that the solvent or diluent medium used in 40 the products is composed predominantly of water and that only small amounts of water-miscible or water-dispersible organic solvents are present in addition. With preference the solvent consists solely of water.

45 Examples of water-based products include, in particular, coating materials, impregnating materials, water-based varnishes or paints, printing inks, such as flexographic or inkjet inks, for

example, dispersions such as acrylate or styrene-acrylate dispersions, for example, and also the formulations of such dispersions for use, for example, as wall paint, coating compositions, and textile auxiliaries. Further examples include 5 polyurethane dispersions and their use, for example, to prepare transparent coating materials for wood, paper or coatings on plastic.

The polymeric biocidal additive employed in the method of the 10 invention is a water-soluble or at least water-dispersible polymer. The polymer is preferably soluble in water.

As monomer (a) the polymer used in accordance with the invention contains from 30 to 100 mol% of styrenesulfonic acid, based on 15 the sum of all the monomeric units. The monomer is preferably 4-styrenesulfonic acid, but can also be 2- or 3 styrenesulfonic acid or a mixture of the three isomers. With preference the polymer used in accordance with the invention contains from 30 to 98 mol% of styrenesulfonic acid, more preferably from 50 to 90 20 mol%, and very preferably from 60 to 80 mol%.

As comonomer (b) use is made of from 0 to 40 mol% of an N-vinylactam and/or N-vinylamine. By way of example it is possible to use N-vinylpyrrolidone, N-vinylpiperidone, 25 N-vinylcaprolactam or N-vinylformamide. Mixtures of different N-vinylactams and/or different N-vinylamines can also be used. Preference is given to N-vinylpyrrolidone and N-vinylcaprolactam, particular preference to N-vinylpyrrolidone. The polymer used in accordance with the invention contains preferably from 2 to 30 40 mol% of the comonomer (b), more preferably from 3 to 30 mol%, and very preferably from 5 to 20 mol%.

As an option it is possible to use further comonomers (c) containing olefinically unsaturated groups, which can be 35 polymerized by a free-radical method. Monomers of this kind serve to fine-tune the properties of the polymer. The nature and amount of any further monomer are selected by the skilled worker in accordance with the properties desired for the polymer. In principle it is possible to use any free-radically polymerizable 40 monomers subject to the proviso that no unwanted properties result. In particular the polymer must remain soluble or dispersible in water. Monomer (c) preferably comprises derivatives of unsaturated carboxylic acids, such as (meth)acrylic esters, acrylamides or acrylonitrile. Examples 45 include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, and the esters of (meth)acrylic acid that

derive from the isomeric butanols, and also hydroxyethyl (meth)acrylate, hydroxymethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl acrylate and hydroxybutyl (meth)acrylate. Suitable monomers further include unsaturated 5 alcohols and amines and derivatives such as for example vinyl alcohol, vinyl acetate, vinyl propionate, vinyl stearate, vinyl benzoate, vinyl maleate, vinyl butyral, allyl phthalate, and allylmelamine. It is also possible, furthermore, to use ethylenically unsaturated hydrocarbons, such as ethylene, 10 propylene or styrene, for example. It is of course also possible to use mixtures of different comonomers (c).

In one particular embodiment the comonomers (c) may be comonomers which in addition to an ethylenically unsaturated group contain 15 crosslinkable groups. When comonomers of this kind are used the polymers obtained have additional functionalities which can be used for the purpose of crosslinking. One possible example in this case is acetoacetoxyethyl methacrylate.

20 The polymer used in accordance with the invention normally contains from 0 to 30 mol% of the comonomer (c), preferably from 1 to 20 mol%, and more preferably from 5 to 15 mol%.

The sum of the monomers (a), (b), and (c) present in the polymer 25 amounts to 100 mol%.

The free-radical polymerization of the monomers presents no particular features and can be carried out in accordance with techniques known in principle to the skilled worker, for example, 30 as an emulsion, dispersion or solution polymerization or inverse suspension polymerization or by polymerization in bulk. Preference is given to polymerization in solution, as described by EP-A 130 789 for example.

35 The weight average of the molecular weight is normally from 10 000 to 500 000 g/mol, although in certain cases good results may also be achieved outside of this range. The weight average is preferably from 15 000 to 300 000 g/mol and more preferably from 20 000 to 200 000 g/mol. The polydispersities  $M_w/M_n$  are normally 40 between 1.3 and 10 and are preferably < 5 and more preferably < 3. Nevertheless, acceptable results may still be achieved even outside of these ranges.

The polymers used for the method of the invention are 45 water-soluble or water-dispersible. The sulfonic acid groups of the styrenesulfonic acid units in the polymer may be in the form of free acid groups. Alternatively some or all of them may be

converted into salts. Alkali metal salts are preferred, and sodium salts particularly so. This also applies to any comonomers (c) in the polymer that contain acid groups.

5 The biocidal additive is added to aqueous industrial systems - that is, for example, to the refrigeration circuit or heat exchanger circuit, or else to the product, i.e., for example, to the aqueous dispersion. The additive can be added as it is. Preferably, however, it is the concentrates that are added. The  
10 skilled worker will also ensure that the biocide is distributed as uniformly as possible in the product or system under protection. The concentration used is guided by the desired end use and is chosen appropriately by the skilled worker. Thus for long-term prevention the skilled worker will generally use only a  
15 relatively small amount of the biocidal additive. Where a sudden infestation with microorganisms is to be controlled the skilled worker will select a higher concentration.

The biocidal additive is normally used in amounts of from 0.001  
20 to 5% by weight. From 0.005 to 1% by weight is preferred, and from 0.01 to 0.5% by weight particularly preferred.

These concentrations refer to the use of the biocidal additive. It will be appreciated that concentrates of the polymer are  
25 preparable, too, which for use are first diluted to the desired concentration.

The water-soluble or water-dispersible polymers used in accordance with the invention can be employed as the sole  
30 biocidal additive. They are effective not only against bacteria but also against fungi and algae. Naturally, mixtures of different water-soluble or water-dispersible polymers as defined above can also be used. A further possibility is to use other biocidal additives or other auxiliaries, provided that no  
35 unwanted effects occur.

The polymers used in accordance with the invention are particularly suitable for protecting aqueous dispersions and products in which the aqueous dispersions are used. Examples of  
40 suitable dispersions include in particular dispersions based on acrylates, such as styrene acrylate dispersions, and also butadiene-styrene dispersions or polyurethane dispersions. The polymers can be added to such dispersions without giving rise to adverse effects. For example, the dispersions protected in  
45 accordance with the invention can be spray dried without substantially lessening the effect of the biocide.

The abovementioned polymer can also be utilized in a method of protecting articles by applying an antimicrobial, aqueous composition to the surface of the article.

- 5 The aqueous composition for coating comprises water or a predominantly hydrous solvent mixture, the biocidal additive outlined above, and, optionally, one or more binders and also further auxiliaries and additives.
- 10 "Predominantly hydrous" means that the greater part of the solvent mixture is composed of water and that only smaller amounts of one or more additional cosolvents are present, these amounts being not more than 25%, preferably not more than 15%, and very preferably not more than 5% by weight, based on the
- 15 amount of all of the solvents. Suitable cosolvents ought to be miscible with water and can in particular be alcohols.

The biocidal additive is normally present in amounts of from 0.001 to 5% by weight. From 0.005 to 1% by weight is preferred, 20 and from 0.01 to 0.5% by weight particularly preferred.

The composition preferably includes a binder. The binder can be a water-soluble binder. An example that may be mentioned is polyvinyl alcohol. Preferably, however, the binder is one which 25 although not soluble in water is dispersible therein, such as an acrylate dispersion, for example.

The composition may further comprise suitable additives and auxiliaries, such as dispersing auxiliaries, further biocides, 30 adhesion promoters or dyes, for example. It is prepared by thoroughly mixing all of the components of the composition with the solvent.

In particular the composition may also comprise a crosslinker or 35 a system of crosslinkers. The nature of the crosslinker is dependent on the envisaged use of the composition. For example, the crosslinker can be one which triggers crosslinking on contact with atmospheric oxygen. Alternatively it may be a crosslinker system which can be cured thermally or photochemically. The 40 components of the crosslinker may be present in the composition from the start. However, it is also possible not to add crosslinking components until shortly before the composition is used.

45 The composition is applied to the article to be protected, by coating, spraying or dipping, for example. The solvent is subsequently removed, generally simply by evaporation. If

crosslinking is desired it can be triggered by irradiation or heating, or takes place as soon as the composition is applied to the article which is to be protected.

- 5 The composition can be used for coating for both indoor and outdoor applications. The additive does not alter the primary end properties of the coating, but merely makes the coating more stable in the long term to microbial, fungal and/or algal infestation.

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The examples which follow illustrate the invention.

Example 1:

15 Test in a styrene/acrylate dispersion

Test procedure:

20 ml of each sample were inoculated with 0.2 ml of the  
20 individual microbial suspensions, homogenized, and incubated at 25°C. The microbe count was made immediately and after 14 and 28 days. This was done by plating out the inoculated sample in appropriate dilutions onto CASO agar with disinhibitor, using spatulas, or mixing the inoculated sample with the agar as a pour plate. The inoculated sample was diluted by homogenization with Caso broth + No. 3 and incubation for 30 minutes in a waterbath at 40°C. For detection of the bacteria, CASO agar plates were incubated at 30-35°C for 3-5 days.

30 Testing procedure:

For the tests the biocidal additive used was sodium polystyrenesulfonate with an  $M_w$  of 20 000 g/mol.

35 A commercial aqueous styrene/n-butyl acrylate polymer dispersion with a solids content of 50%, a particle size of 170 nm, and a viscosity of 400 mPas (Acronal S 728 from BASF) was doped with either 500, 1000 or 2000 ppm of biocidal additive. Adding the biocide did not alter the properties of the dispersion. A 40 microbial exposure test was carried out in accordance with the test procedure described above using Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus aureus. The results are set out in table 1.

Sam- ple	Concentration of biocidal additive [ppm]	Time	Escher- ichia coli	Pseudo- monas aeruginosa	Staphylococcus aureus
5	0	no biocide	48 h	$10^4$	$10^{-5}$
	1	500	24 h	6000	0
	2	500	48 h	0	0
	3	1000	24 h	8000	0
	4	1000	48 h	0	0
	5	2000	24 h	3600	100
10	6	2000	48 h	0	0

Table 1: Results of the tests of example 1

## Example 2:

- 15 For the tests the biocidal additive used was sodium polystyrenesulfonate/N-vinylpyrrolidone (90/10) with an  $M_w$  of 30 000 g/mol.
- 20 A microbe-free aqueous solution was dosed with either 10, 100 or 1000 ppm of the biocidal additive. A microbe exposure test was carried out in accordance with the test from Ph. Eur. 3, 2000 (5.1.3) using Escherichia coli, Pseudomonas aeruginosa, and Staphylococcus aureus. The results are set out in table 2. After 25 3 months at room temperature the samples were measured again, but no increase in the microbe count was found.

No.	c [ppm]	pH	Escher- ichia coli	after 14 days	Pseudo- monas aeruginosa	after 14 days	Staph- ylo- coccus aureus	after 14 days
30	1	10	7	$4.7 \cdot 10^5$	<10	$4.7 \cdot 10^5$	<10	$4.7 \cdot 10^5$
	2	100	7	$2.3 \cdot 10^5$	<10	$2.3 \cdot 10^5$	<10	$2.3 \cdot 10^5$
35	3	1000	7	$1.4 \cdot 10^5$	<10	$1.4 \cdot 10^5$	<10	$1.4 \cdot 10^5$

Table 2: Results of the tests of example 2

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## Example 3:

## Spray drying of a dispersion

- 5 For the drying test the biocidal additive used was sodium polystyrenesulfonate/N-vinylpyrrolidone (95/5) with an  $M_w$  of 20 000 g/mol in a 20% strength aqueous solution of a vinylpyrrolidone/vinyl acetate copolymer (monomer ratio about 55/65;  $M_w$  45 000-70 000 g/mol) (Kollidon® VA 64, BASF AG).

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- The solution was processed in a one-nozzle spray dryer at entry temperatures of more than 140°C. The concentration of the polymeric biocide was found to be the same within the bounds of determination errors. A repeat inoculation as described in 15 example 1 showed the biocidal activity to be unchanged.

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Biocide concentration [%]	0.01	0.1	1
Residual moisture content [%]	2.0	2.1	2.4
Concentration in the powder [%]	0.05	0.49	5.05
Color	colorless	colorless	colorless
pH	6.1	6.2	6.3
Solids content [%]	98	97.9	97.6

Table 3: Results of example 3 (amounts in % by weight)

## 25 Example 4:

## Test in milk

- 30 A sample of milk was treated with 0.01% by weight of the sodium polystyrenesulfonate described in example 1. After 5 days of closed storage at room temperature the sample was still stable (microbe count, appearance, odor).

- 35 A comparative sample showed marked microbial infestation after just 24 hours of closed storage at room temperature.

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